INHIBITION OF MILD STEEL BY ZINC 1-HYDROXYETHANE-1, 1 DIPHOSPHONIC ACID (HEDP) MIXTURES

H S AWAD AND S TURGOOSE
CORROSION AND PROTECTION CENTRE
UMIST
PO BOX 88
MANCHESTER, UK

1-Hydroxyethane-1,1-Diphosphonic Acid (HEDP) has been widely used as a corrosion inhibitor for cooling water treatments. The inhibition mechanism by HEDP is not entirely clear; some workers [1] suggest that it acts as an anodic inhibitor of medium efficiency for mild steel in neutral oxygen containing solutions but only at low concentrations (< 20 ppm, 10^{-4} M). The addition of some bivalent cations such as zinc and calcium ions significantly enhances the inhibition effect of HEDP [2,3]. However, although it is well known that the effective inhibition provided by zinc-HEDP mixture is due to metal-phosphonate complex, no studies have been reported regarding the inhibitive nature of the zinc-HEDP complexes.

Calculations of the stability of the zinc-HEDP complexes that based on the dissociation constants of the HEDP and the stability constants of the possible Zn^{2+}-HEDP complexes [4] have been carried out. The results show that of 14 species present, only five major species, H_2L^{2-}, HL^{3-}, ZnL^{2-}, $Zn_2H_{-1}L^{-}$ and Zn^{2+}, exist in solution of zinc and HEDP. The relative predominance depends on several variables such as solution pH, total zinc and total HEDP concentrations.

From the results of the calculations for $zinc_{total} = 20$ ppm and $L_{total} = 32$ ppm (0.00017 M) for varying the pH it is found that the **2:1**, zinc:HEDP complex, $Zn_2H_{-1}L$ is the most stable complex over a wide range of pH, 5-11. Free phosphonate and the 1:1 complex, ZnL, only exist in significant quantities at lower pH.

Linear Polarization Resistance, Polarization Curves and EIS Impedance have been combined with surface examination and analytical techniques (Scanning Electron Microscopy SEM and X-ray Photoelectron Spectroscopy XPS) to investigate the effect of zinc-HEDP mixture on the corrosion inhibition of mild steel. This has been studied with different pH, zinc contents, HEDP and chloride levels, and has been correlated with the solution complexes present.

It is found that the mixture (20 ppm zinc - 32 ppm HEDP) performs well, in the chloride free solutions, over a wide range of pH, 6.5-9.5, whereas its inhibition effect significantly reduces at lower pH, 4.5. The solution speciations showed that this inhibition is attributed to the presence of the 2:1 $Zn_2H_{-1}L$ complex, at a sufficient level, 0.00015 M, and to the absence of the aggressive free phosphonate. However in the acidic pH, 4.5, HEDP exists in the free form, which is found to be aggressive and can lead to loss of inhibition. In addition, the level of the inhibitive 2:1 complex at this pH is far below the optimal level for protection

The results indicate that the 2:1 zinc:HEDP complex can behave as an anodic, passivating, inhibitor at concentrations as low as 0.00015 M. This passivation is considered to be due to the local formation of an iron salt of the inhibitive, complex, anion, as with other anodic inhibitors. This passivity is prevented by the presence of sufficient chloride, and also by the presence of free phosphonate. The critical chloride concentration in these studies is approximately ten times higher than the complex concentration, in molar terms, and passivity can be obtained at complex concentrations of 0.00015 M (20 ppm zinc), in the presence of 0.0015 M chloride (53 ppm).

The inhibition effect of the zinc-HEDP mixture has also been investigated at varying zinc concentrations (0-100 ppm). The inhibition by this mixture was studied at pH 7.5 in the presence of low levels of chloride, < 0.003 M (100 ppm) with 70ppm HEDP.

Results show that the efficiencies obtained form EIS are in agreement with those obtained from the linear polarization resistance measurements. The zinc-HEDP mixture shows a poor protection at Zn:HEDP molar ratio lower than 2 which is found to be due to the increase in the chloride:inhibitor molar ratio beyond the critical ratio for protection, as well as to the presence of free phosphonate.

Good protection is achieved with molar ratios greater than 2:1, i.e. with free Zn^{2+}, and efficiency reaches a maximum of 96% at 2.7 molar ratio (corresponding to 60 ppm zinc). The inhibitor at this ratio significantly reduces the anodic current and affects the mechanism, and rate, of the cathodic process.

However the inhibitor efficiency declines significantly with molar ratio greater than 2.7, the anodic effect is absent while there is a significant effect on the cathodic, oxygen reduction, reaction. This could be due to the formation of a thick surface film that prevents the anodic effect, perhaps via restriction of access of the inhibitor and/or oxygen to the underlying metal. This supported by the SEM analysis, which showed a clear evidence of a visible film on the specimen surface.

References

1. E.Kalman B.Varhegyi, I.Bako, I.Felhosi, F.H.Karman, and A.Shaban, J.Electrochem Soc.,141, 3357(1994).
2. Y.I.Kuznetsov, Organic Inhibitors of Corrosion of Metals, Plenum Press, New York (1996).
3. E.Kalman, in Corrosion Inhibitors, EFC Publication No 11, Institute of Materials, London (1994).
4. M.I.Kabachnik, R.P.Lastovskii, T.Ya.Medved, V.V.Medynstev, I.D.Kolpakaova, and N.M.Dyatlova, Proc. Acad. Sci.(U.S.S.R) 177, 1060 (1967).

Table I

Zinc Conc ppm	Molar ratio	$Zn_2H_{-1}L$ ppm	η DC	η DC	E_{corr} mV
20	0.9				
35	1.6				
43	2				
60	2.7				
80	3.7				
100	4.6				